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XI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

THE ATOMIC WEIGHT OF ANTIMONY.

PRELIMINARY NOTICE OF ADDITIONAL EXPERIMENTS.

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Presented March 10, 1880.

IN our previous paper on this subject,* we gave our reasons for the opinion, since fully confirmed, that the bromide of antimony is the most suitable compound of this element, as yet known, for determining its atomic weight; and the results of fifteen analyses of five different preparations of the bromide were published, which gave for the atomic weight in question the mean value 120.00 with an extreme variation between 119.4 and 120.4 for all the fifteen analyses, and between 119.6 and 120.3 for the six determinations in which we placed most confidence. The antimonious bromide used in these determinations was purified first by fractional distillation, and secondly by crystallization from a solution in sulphide of carbon. In the crystallized product thus obtained, the bromine was determined gravimetrically as bromide of silver in the usual way. Although it seemed at the time that the results were as accordant as the analytical process would yield under the unfavorable conditions, which the presence of a large amount of tartaric acid in the solution of the bromide of antimony necessarily involved; yet it was obvious that the agreement was far from that which was desirable in the determination of an atomic weight, and our chief confidence in the accuracy of the mean value —

* These Proceedings, Vol. XII. page 1.

independently of its remarkable agreement with previous results — was based on the fact that the known sources of error tended to balance each other. Hence our conclusions were stated with great caution, and the hope was expressed that after a more thorough investigation of the subject we might be able “to return to the problem with such definite knowledge of the relations involved as will enable us to obtain at once more sharp and decisive results than are now possible.” Unfortunately this investigation has been delayed by causes beyond our control.

In our previous paper, we described a simple apparatus which we devised for subliming iodide of antimony; and in a note to the paper we stated that we were applying the same process to the preparation of the bromide of antimony, and that it promised excellent results. Our expectations in this respect have been fully realized, and the product leaves nothing to be desired either as regards the beauty or the constancy of the preparation. The fine acicular crystals are perfectly colorless, and have a most brilliant silky lustre. With ordinary precautions they can be kept indefinitely without change, and it is easy therefore to determine the weight of the material analyzed to the tenth of a milligramme.

We have carefully studied the causes of error involved in the analytical process of determining bromine in an aqueous solution of bromide of antimony and tartaric acid by the usual gravimetric method. These causes we propose to discuss in a future more extended paper. In this preliminary notice, we have only space to state that we have satisfied ourselves that the small differences between the results previously obtained arose wholly from the analytical process, and not from any want of constancy in the material analyzed; and further that these sources of error are to a very great extent under control. Moreover, we have found that the volumetric determination of bromine by silver was not materially affected, if at all, by the same causes. We have thus been led to devise a mode of testing the atomic weight of antimony, which, while it has all the advantages of the gravimetric method previously employed, is free from its sources of error.

If the atomic weight of antimony were 122.00, it would require 1.7900 grammes of pure silver to precipitate the bromine from a solution of 2.0000 grammes of antimony bromide, while if the atomic weight of antimony were 120.00 it would require 1.8000 grammes of silver. Now it is easy to estimate volumetrically $\frac{1}{100}$ of this difference with great certainty. We therefore prepared with great care

a button of *pure* metallic silver, which we annealed and rolled out to a thin ribbon. We then weighed out from two to four grammes of bromide of antimony, prepared by sublimation as described above, and dissolved this salt in an aqueous solution of tartaric acid, which we then transferred to a litre flask and diluted to about 500 cubic centimetres. We next very accurately weighed out a quantity of silver slightly less than that which calculation showed was required for complete precipitation. This silver was dissolved in nitric acid, and the solution having been evaporated to dryness over a water bath, the silver salt was washed into the flask containing the bromide of antimony. As soon as the supernatant liquid had cleared, the small additional amount of a normal silver solution required to produce complete precipitation was run in from a burette, and measured with the usual precautions. We used no extraneous indicator, because it was important not to introduce any possibly new disturbing element into the experiment, and in the titration of bromine with silver the normal and familiar phenomena, which mark the close of the process, furnish a very sharp indication. The details of one of the determinations were as follows:—

The weight of the bromide of antimony used amounted to 2.5032 grammes. To precipitate the bromine from the solution of this material 2.2404 grammes of silver would be required if $Sb = 122.00$ and 2.2529 if $Sb = 120.00$. We weighed out, with as much accuracy as if we were adjusting a weight, the smaller of these two quantities of metallic silver, and after dissolving the pure metal in pure nitric acid, evaporating the solution to dryness and redissolving in water, we added at once the whole of this silver solution to the litre flask containing the solution of bromide of antimony, in the manner described above. It was then found that $12\frac{4}{10}$ cubic centimetres of a normal silver solution (one gramme of silver to the litre) were required to complete the precipitation. It will be seen that the weights of the bromide of antimony and silver used could be thus determined with the most absolute precision, and we have the greatest confidence in these values to the $\frac{1}{10}$ of a milligramme. Moreover, it will be noticed that the volumetric method is only used to estimate the difference in the atomic weight which has been in question, and that if the method were only accurate to the $\frac{1}{10}$ of the quantity to be measured it would give us the value of the atomic weight within $\frac{2}{10}$ of a unit; while if, as we had reason to believe, the process was accurate within one per cent, it would fix the atomic weight within $\frac{2}{100}$ of a unit.

By the method just described, the following results were obtained. The letters *a* and *b* indicate different preparations.

Wt. of Sb Br ₃ taken.	Total Wt. of Ag used.	Per Cent of Br Ag = 108 Br = 80.	Corresponding value of Sb.
<i>a</i> 1. 2.5032	2.2528	66.6643	120.01
<i>a</i> 2. 2.0567	1.8509	66.6620	120.02
<i>a</i> 3. 2.6512	2.3860	66.6644	120.01
<i>b</i> 4. 3.3053	2.9749	66.6696	119.98
<i>b</i> 5. 2.7495	2.4745	66.6653	120.01
Mean value,		66.6651	120.01
Mean value of fifteen gravimetric de- terminations previously published,		66.6665	
Theory Sb. 120 requires		66.6666	
,, Sb. 122 ,,		66.2983	

In order still further to control the work, we collected the bromide of silver formed in the last two determinations, washing the precipitate with the precautions which experience had shown to be necessary, and determining its weight, first, after drying at 150° C., and, secondly, after heating to incipient fusion. In *b* 6 there was a loss of $\frac{1}{10}$ of a milligramme; in *b* 7 a loss of $\frac{2}{10}$ of a milligramme only at the second weighing. This is an absolute proof that there could be no sensible occlusion of any tartaric acid or any tartrate by these precipitates, and, as stated in our original paper, the same test was frequently applied, although not always, in our previous determinations. It is also evident that these last experiments give us two essentially distinct determinations of the atomic weight, although the materials employed were identical with those of *b* 4 and *b* 5.

Wt. of Sb Br ₃ taken.	Wt. of Ag Br determined.	Per cent of Bromine Ag = 108 Br = 80.	Corresponding value of Sb.
<i>b</i> 6. 3.3053	5.1782	66.665	120.01
<i>b</i> 7. 2.7495	4.3076	66.667	120.00
Mean value,		66.666	120.00

Lastly, it is obvious that these gravimetric determinations, taken in connection with the corresponding volumetric results, give us the most conclusive evidence of the purity, both of the metallic silver used, and

also of the bromine in the bromide of antimony, which is the basis of this atomic weight investigation. By comparing *b* 6 and *b* 7 with *b* 4 and *b* 5 respectively, we obtain the following data :—

1. 2.9749 gram. of silver gave 5.1782 gram. bromide of silver.
2. 2.4745 " " " 4.3076 " " "

Hence it follows that, as shown by these experiments, the proportions of the silver to the bromine were respectively :—

	1.	108.00	Silver to	79.99	Bromine.
	2.	108.00	" "	<u>80.01</u>	"
Mean value,		<u>108.00</u>	" "	<u>80.00</u>	"

This is the ratio of the atomic weight of silver to that of bromine, and corresponds to the second decimal place with the determinations of Stas as well as with those of Dumas.

In conclusion it gives us pleasure to express our obligations to Mr. G. De N. Hough and Mr. G. M. Hyams, two students of this laboratory, who have greatly aided us in the experimental work of this investigation.